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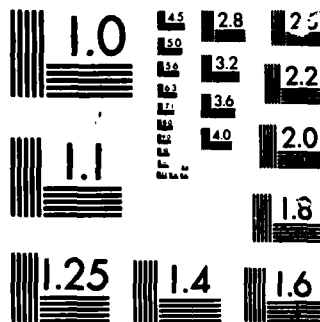
LIGHT SCATTERING STUDIES OF MOLECULAR DYNAMICS IN
MOLECULAR CRYSTALS LIQU. (U) COLORADO STATE UNIV FORT
COLLINS DEPT OF CHEMISTRY E R BERNSTEIN 02 APR 85
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FINAL TECHNICAL REPORT

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"LIGHT SCATTERING STUDIES OF MOLECULAR DYNAMICS IN MOLECULAR CRYSTALS,
LIQUID CRYSTALS AND POLYMERS FOR APPLICATIONS IN CHEMICAL DEFENSE"

Principal Investigator

Elliot R. Bernstein
Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

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MATTHEW J. KIEPPE

Chief, Technical Information Division

Progress Report -

A great deal of work has been accomplished during this last four year funding period. A total of 16 papers have appeared in the literature dealing with both the theoretical and experimental (light scattering) investigation of phase transitions and critical phenomena in simple molecular solids. Based on this work we are now able to progress to the more complicated, extended crystal systems presently under consideration. The past year was a critical one in our laboratory - it served as a transition between temperature dependent simple molecular crystal studies and pressure-temperature studies of perovskite, polymer, and liquid crystal systems. In the next few pages we present a review of this recent activity.

In order to save space and time, it will be assumed throughout this presentation that the reader is vaguely familiar with the basic concepts, methods, and techniques of our previous phase transition investigations. In particular, the theory and practice of light scattering studies in general, the basic treatment of phase transitions and critical phenomena, and the fundamentals of Landau mean field theory will not be dealt with in any detail in the rest of the proposal. Many of those and other points can be found in our early papers and in the cited literature therein.

1. Critical Phenomena at the Phase Transition in Benzil

New Brillouin scattering data have been obtained for benzil single crystals near the phase transition at 83.5K. These data demonstrate that for the c_{11} governed longitudinal acoustic (LA) mode at ~15 GHz, critical fluctuations are quite large near the phase transition and dominate the behavior of this mode within +40K of the transition. These observations are analyzed in terms of four contributing soft modes; an optical soft mode and two transverse acoustic (TA) soft modes at the zone center, and a zone boundary M-point soft mode. It is found that the zone boundary mode is the

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major contributor to the width and elastic constant anomalies of the LA mode. Calculations of these properties support the above conclusions. Critical exponents are evaluated for Δc_{11} and $\Delta \Gamma_a$, the critical contributions to the elastic constant and width of the c_{11} governed LA mode, based on the experimental data. This is the first molecular crystal for which such a complete study of critical behavior has been carried out and one of the few times Brillouin scattering has been so used for any system.

2. Mean Field Theoretical Studies of Ferroelastic Transitions in Molecular Crystals

A mean field approach to the dynamics of structural phase transitions in molecular crystals has been developed. The approach is based on a description of the rotational and translational molecular motions, and the coupling between them, in terms of generalized susceptibilities. Two models for the orientational susceptibility are used. One is a classical description in terms of two-dimensional rotors, the other a two dimensional anharmonic oscillator model. The specific example considered is sym-triazine. In this crystal, molecules experience a very strong orienting field which restricts the molecular rotational motion to libration. The coupling between the molecular rotations and translations is shown to lead to a softening of acoustic phonons, which has considerable anisotropy in reciprocal space. An approximate solution for the high temperature phase is found to be in good agreement with experiments.

3. Liquid Crystal Studies: $\text{Na}_2\text{SO}_4/\text{Na}$ decyl sulfate/decanol/ H_2O

Some very real practical progress has been made this past year with the sodium decyl sulfate/decanol/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ liquid crystal project. We believe we have finally solved most of the last few remaining problems with this system and now know the proper directions to pursue. The main areas of

progress are in the preparation of solutions, composition of solutions, and producibility of light scattering data.

Sample preparation has been carefully considered in terms of the light scattering studies and we find that filtration of the components with a .22 μ filter before putting the sample together is important for reproducible results and clear samples. Once the samples are made, dust is not readily included in the material and care with the samples is much less important. Apparently, the micelles can form around included dust and particulate matter, which then become an integral part of the solution.

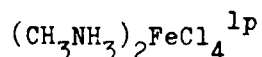
A number of studies we have carried out this year have dealt with the importance of various components for the overall solution behavior. In particular, Na_2SO_4 has been shown to be an essential constituent of the liquid crystal system. We have varied the liquid crystal composition from 0 to 7% Na_2SO_4 with several dramatic changes observed. First, the nature of the light scattering changes significantly with changes in Na_2SO_4 . Rayleigh correlation functions become much weaker and have a much faster associated relaxation time as the Na_2SO_4 concentration goes to zero. The micelle size and micelle-micelle interactions must be a very strong function of the ionic strength of the solution. This finding implies and underscores the overriding importance of the aqueous phase of the liquid crystal for its fundamental physical and structural properties. Second, the liquid crystal structure is clearly different as a function of Na_2SO_4 concentration: large changes in viscosity are observed as the amount of Na_2SO_4 in solution is varied. The micelle size and intermicelle interactions are essentially coupled to the solution ionic strength. Third, the light scattering data (both Rayleigh and

Brillouin) are much more reproducible and have a much better signal to noise ratio if low (<2%) Na_2SO_4 concentrations are used. Thus, in addition to all the other aspects of the contributions of Na_2SO_4 to the properties of lyotropic liquid crystals, Na_2SO_4 apparently enhances the dynamics of the micelle motion and causes micelle size, geometry, structure, and/or concentration to fluctuate. A number of the new directions taken in the next few years with this system will be an outgrowth of these important and interest findings (e.g. new salt components, solvent properties as a function of salt concentration, pressure variation, etc.)

Much too much work has been published on liquid crystals in general and even lyotropic liquid crystals in particular to provide a discussion of the various phases and systems in a short paragraph. A recent paper dealing with Rayleigh scattering from a decyl ammonium chloride, NH_4Cl , H_2O system indicates that many similarities exist between the nematic and lyotropic liquid crystals: structural similarities may also exist between this system and the perovskite layer compounds. This system appears to be somewhat different from the quaternary one that we have been studying due to its apparent insensitivity to ionic strength. Comparison between the two systems will be important for determining the effects of the various constituents on the overall liquid crystal behavior: the effects on the light scattering spectra (Rayleigh, Brillouin, and Raman) of fluctuations in micelle size and shape may be important for this comparison. An additional study has appeared reporting portions of the phase diagram for the sodium decyl sulfate/decanol/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ system of interest: this will, of course, be useful for choosing appropriate sample concentrations and temperature ranges.

Most of the important advances of the past 15 years in the study of lyotropic liquid crystals (e.g., phase diagrams, structures, orientational properties in magnetic and electric fields, and others) have been discussed. Since we do not have extensive data of our own to present for comparison, a review of these properties would not be particularly useful at this time.

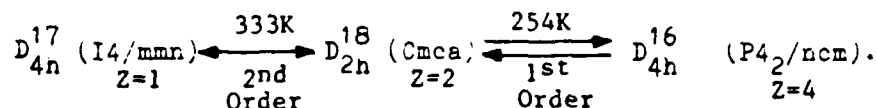
4. Brillouin Scattering Study of the Successive Phase Transitions in



Since this system is new to our work and has produced some very interesting results, it is appropriate to spend some time introducing it and making the basic aspects of its properties clear. Our interest in the system $[\text{RNH}_3]_2\text{MCl}_4$, in general, stems from numerous phase transitions, critical behavior, and the hydrocarbon chain order-disorder behavior. The parallels drawn between these model layer compounds and the more complicated liquid crystal and polymer systems may be important for a complete understanding of the latter.

Methmonium iron chloride, $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$ (MAFeCl) possesses a perovskite layer structure which consists of infinite sheets of corner sharing divalent transition metal-halogen octahedra. The crystal exhibits quasi-two-dimensional antiferromagnetic order in the (001) plane but weak ferromagnetic ordering along the [001] direction below 93K. In addition to the magnetic transition at low temperature, this system also possesses successive structural phase transitions. These have been studied by means of lattice dynamics and far infrared spectroscopy, birefringence, x-ray and neutron diffraction, specific heat and ultrasonic sound velocity measurements, and ultrasonic attenuation measurements.

The sequence of successive phase transitions is quite unusual, in general, although common throughout the series:



According to a group theoretical analysis of the successive phase transitions in $(CH_3NH_3)_2MCl_4$ (with $M = Mn$ and Cd), this sequence can be explained by successive freezings of a two dimensional order parameter (η_1, η_2) at the Brillouin zone boundary X-point (D_{2h} symmetry) of the D_{4h}^{17} high symmetry high temperature "parent" phase.

The D_{4h}^{17} phase is described by the trivial solutions to the Landau free energy equation, $\eta_1 = \eta_2 = 0$. The solutions with $\eta_1 \neq 0$, $\eta_2 = 0$ and $\eta_1 = 0$, $\eta_2 \neq 0$ lead to the D_{2h}^{18} phase and account for twin domains which are, more precisely, ferroelastic if the strain e_6 is included into the Landau free energy. The coordinate system for the D_{2h}^{18} phase is rotated by 45° about the D_{4h}^{17} fourfold axis. Since only one arm of the star is involved in this second order phase transition, the unit cell size is expanded by only a factor of two.

Solutions with $\eta_1 = \eta_2 \neq 0$ and $\eta_1 = -\eta_2 \neq 0$ lead to the D_{4h}^{16} phase. These solutions correspond to antiphase domains and the D_{4h}^{16} phase is nonferroelastic. The new tetragonal unit cell is primitive, with a coordinate system rotated by 45° with respect to the high temperature D_{4h}^{17} coordinate system. Since in this case both arms of the star of \underline{K} are involved in the phase transition, the

case both arms of the star of \underline{K} are involved in the phase transition, the unit cell is fourfold expanded with respect to the D_{4h}^{17} parent phase unit cell.

A new set of elastic constants for $MAFeCl$, obtained by Brillouin scattering, have been determined this past funding period. Our specific findings can be summarized as follows:

i. Based on a comparison between low frequency ultrasonic results and the present Brillouin results, the elastic constant c_{66} evidences strong frequency dependent critical softening in the D_{4h}^{17} phase. There appears to be little residual critical fluctuation softening in this phase at ~ 10 GHz.

ii. The elastic constant c_{66} possesses a minimum about 15K below the D_{4h}^{17} - D_{2h}^{18} phase transition temperature. The c_{66} elastic constant smoothly changes in the immediate vicinity of the phase transition. The existence of the minimum and the smooth behavior suggest that critical fluctuations and a Landau-Khalatnikov process in the D_{2h}^{18} phase are responsible for the c_{66} anomalous behavior at this transition.

iii. At the D_{2h}^{18} - D_{4h}^{16} phase transition c_{66} suddenly jumps from the D_{2h}^{18} phase value ($\sim 6 \times 10^9$ N/m²) to the extremely low D_{4h}^{16} phase value ($\leq 0.5 \times 10^9$ N/m²). Below this transition c_{66} rapidly increases as the temperature decreases. The Brillouin data and ultrasonic results are quite similar in the D_{4h}^{16} phase and no dispersion is suggested for this phase.

iv. The other elastic constants, c_{11} , $(c_{11} + c_{12})/2$, and c_{44} , show no clear anomalies at these phase transitions.

The c_{66} elastic anomalies can be treated within the framework of Landau theory. In addition to the two dimensional X-point order parameter, a new

secondary order parameter at the Z-point can be introduced. The secondary order parameter is important for $D_{2h}^{18}-D_{4h}^{16}$ phase transition because it couples linearly to the X-point order parameter components and becomes finite in the D_{4h}^{16} phase. In a sense, an unrealized phase transition, due to the secondary order parameter, has been introduced in addition to the X-point transition.

Based on the X-Z point model, the sequence of successive phase transitions $D_{4h}^{17}-D_{2h}^{18}-D_{4h}^{16}$ can be explained. Moreover, a step anomaly at the $D_{4h}^{17}-D_{2h}^{18}$ transition, the large discontinuity at the $D_{2h}^{18}-D_{4h}^{16}$ transition and the $(T_2-T)/(T_3-T)$ dependence of the elastic constant in the D_{4h}^{16} phase observed in ultrasonic experiments can be successfully derived. Although this treatment can explain the essential feature of the c_{66} anomalies, it does not account at present for the critical anomaly observed around the $D_{4h}^{17}-D_{2h}^{18}$ phase transition.

Dynamics of the critical fluctuations (dispersion) have been observed by Brillouin scattering; unfortunately, the c_{66} elastic constant could only be indirectly determined and the results are not precise enough at this time for a detailed discussion of the dynamics of the critical anomaly.

5. High Pressure Studies of Benzene

For the last eight months, we have also been engaged in high pressure Raman, Brillouin, and Rayleigh scattering studies of benzene in a diamond anvil cell. While these techniques were new to us and required some laboratory skills development, we are now able, routinely, to load benzene and follow its Raman spectrum within a few cm^{-1} of the laser line up to 150 kbar in small volume cells ($.1 \text{ mm}^3$). We are continuing these investigations in

order to obtain a better picture of this simple model system for which accurate atom-atom potentials have been obtained. Since these studies overlap with published data on benzene, they represent a useful test of our experimental high pressure spectroscopic techniques. In addition, at pressures above 90 kbar, new Raman bands are observed at ca. 150 cm^{-1} . These features indicate that a new phase has appeared. We are currently refining these results. Brillouin spectra are more difficult to obtain: a new large volume cell ($.5\text{ mm}^3$) designed for 90° access to the scattered light is currently being employed. Weak benzene Brillouin signals have been observed for the low pressure phase I (0 - 10 kbar).

6. Miscellaneous Crystals - Growth and Preparation

Due to the expansion of our interests and activities into new systems, a good deal of effort has gone into sample handling techniques, development of zone refining capabilities, and construct a number of crystal ovens. At present we have grown single crystal boules of hexamethyl benzene and bi-, ter-, and quater-phenyl. Solution growth of the layer perovskite compounds has begun: C_3 , C_5 , C_9 , C_{10} , C_{11} compounds are now being grown into single crystals from various solvents. Crystalline monomer diacetylenes are also soon to be grown from various solvents.

D. List of Publications -

J.C. Raich and E.R. Bernstein, On the Phase Transition in Sym-Triazine-Mean Field Theory, J. Chem. Phys. 73, 1955 (1980).

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J.C. Raich, E.R. Bernstein, and A. Yoshihara, Theory of Structural Transformations in Orientationally Disordered Crystals, Trans. Am. Cryst. Assn. 17, 1 (1981).

A. Yoshihara, C.L. Pan, J.C. Raich, and E.R. Bernstein, Light Scattering Study of the Phase Transition in Sym-Triazine, J. Chem. Phys. 76, 3218 (1982).

J.C. Raich, A. Yoshihara, and E.R. Bernstein, An Equation of Motion Approach to Ferroelasticity in Sym-Triazine, Molec. Phys. 45, 197 (1982).

A. Yoshihara, J.C. Raich, and E.R. Bernstein, Critical Behavior in Annealed and Unannealed Benzil Crystals, J. Chem. Phys. 77, 2768 (1982).

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E. List of Professional Personnel -

Akira Yoshihara - Postdoctoral Fellow
John C. Burr - Postdoctoral Fellow
Shrikrishna M. Mudare - Postdoctoral Fellow

F. Interactions -

- 1981 - State University of New York, Binghamton
Bell Laboratories
Syracuse University
Wesleyan University
University of Michigan
Michigan State University
Wayne State University
University of California at Riverside
University of California at Irvine
University of Southern California
UCLA, Caltech
- 1982 - Xerox Corporation, Rochester, New York
State University of New York at Buffalo
Temple University (PA.)
University of Rochester
University of Pennsylvania
Dartmouth College
- 1983 - University of Chicago
University of Illinois at Chicago Circle
Naval Research Laboratory, Washington, D.C.
Technical University of Wroclaw, Poland
16th European Congress on Molecular Spectroscopy, Sofia, Bulgaria

G. NONE

H. NONE

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